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Estimation of Silver in the Photographic Fixer Solution by Voltammetric Technique

N.Sathaiyan, P.Adaikkalam and K.V.Venkateswaran

Central Electrochemical Research Institute. Karaikudi-630 006

Spent photographic fixer solution, colour bleach-fixer solution (CBFS) etc are very good sources of silver. In view of escalating cost of silver metal and the compelling need for pollution abatement, it is essential to recover silver from the fixer solution. During the processing of films, 20-25% of silver is left in the black and white films, whereas in the case of colour films essentially all silver is dissolved into the solution. Since, the silver concentration in these solutions are very low (2-5 g/l) it is important to analyse the silver in the solution before and after recovery. Experiments were carried to analyse the silver contents of photographic solutions using cyclic voltammetric technique. Effect of silver concentrations as well as effect of sweep rates were found out in the quick estimation of silver in the photographic solutions. Compared with other methods, this voltammetric technique seems to give silver concentration of photographic solutions in short duration without affecting the nature of the solutions.

Key words: Photographic fixer solution, cathode potential, cyclic voltammetry, silver estimation

Introduction

Still films, motion films (both B&W and colour), X-ray films etc after processing, liberate effluents and are discharged. Silver is recovered from the colour bleach-fix solutions, fixer solutions and papers. The treatment of these photographic solutions reduces environmental pollution and is cost effective due to reusing the silver depleted solutions. During the processing of films, 20-25% of the silver is left in B&W films, while all silver present in colour film is dissolved. The maximum tolerable limit of silver for the sewage in industrial waste is 1.0-0.1 ppm. Several techniques are available for the recovery of silver from photographic processing liquors/wastes[1,2] such as cementation[3], ion exchange[4] and electrolysis [5].

The electrochemistry of photographic fixer solution (ammonium or sodium thiosulphate) is rather complex because of the fact that the sulphur compounds present may undergo a variety of redox reactions which interact with the starting material or themselves to yield a number of related products. The electrochemistry of the CBFS (colour bleach-fix solution) is still more complex due to the additional presence of reactive ferric-EDTA complex [6].

During the bleach fixing of colour films (still) which is a single step, both the reduced silver and the unexposed silver bromide in the film are converted to a soluble thiosulphate complex as

$$Ag^{o} + Fe\text{-}EDTA^{1-} \longrightarrow Ag^{+} + Fe\text{-}EDTA^{2-} \quad \text{.....(1)}$$

$$Ag^{+} + 2(S_2O_3)^{2-} \longrightarrow Ag(S_2O_3)_2^{3-} \quad \text{.....(2)}$$

Hence in order to understand the mechanism and the electrode reactions, cyclic voltammetric technique was adopted using silver containing fixer solutions to identify various products that may be formed during the course of reaction[7]. For getting high pure electrolytic silver from the photographic solutions the current has to be gradually decreased with respect to its silver concentration, otherwise sulphiding will occur. Hence the estimation of silver content in the fixer bath is a must during the course of recovery of silver. Several methods such as chemical analysis[8], colorimetry[9], potentiometry[10] are reported in the literature for this.

These methods have some drawbacks since they involve more than one step and toxic chemicals like sodium sulphide are used which would liberate poisonous gas thus affecting the nature of the solution. Hence silver in the photographic fixer solution was estimated employing cyclic voltammetric technique in which there will be no contamination of solution, no liberation of toxic gas since no other chemicals were added.

Experimental

A three electrode glass cell set up was used for the voltammetric studies with inlet and outlet provision for deaeration with platinum disc (0.28 cm^2 area) as working electrode, platinum black as counter electrode and saturated calomel electrode (SCE) as reference. A Wenking Potentioscan (Model POS-73) and an X-Y Recorder (Rikadenki Model RW-201T) were used.

Emery papers down to 4/0 grade were employed in succession to polish the working electrode, which was then degreased with acetone and finally washed with double distilled water. The synthetic fixer solution consisted of 1-8 g/l silver as sodium thiosulphate complex, 250 g/l sodium thiosulphate and 15 g/l sodium sulphite and the pH was made to 5.0. All investigations were carried out at 30±1 °C. The range of potential scan was from –50 to –500 mV vs SCE.

Results and discussions

Before the estimation of silver in the fixer solution, the solution was subjected to cyclic voltammetric technique, for optimizing the cathode potential to deposit silver without sulphiding and it was scanned between the cathode potentials –50 to –1350 mV. During the electrolysis of fixer solutions, the following reactions[11] may be envisaged.

The cathode reactions are:

$$Ag(S_2O_3)_2^{3-} + e^- \longrightarrow Ag^0 + 2(S_2O_3)^{2-} \quad \text{.....(3)}$$

$$S_2O_3^{2-} + 8H^+ + 8e^- \longrightarrow 2HS^- + 3H_2O \quad \text{.....(4)}$$

$$6H^+ + HSO_3^- + 6e^- \longrightarrow HS^- + 3H_2O \quad \text{.....(5)}$$

$$S_2O_3^{2-} + 2e^- \longrightarrow SO_3^{2-} + S^{2-} \quad \text{.....(6)}$$

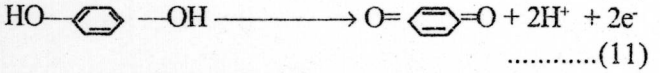
$$2Ag^+ + S^{2-} \longrightarrow Ag_2S \quad \text{.....(7)}$$

The anode reactions are:

$$SO_3^{2-} + H_2O \longrightarrow 2H^+ + SO_4^{2-} + 2e^- \quad \text{.....(8)}$$

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e^- \quad \text{.....(9)}$$

$$SO_3^{2-} + S_2O_3^{2-} \longrightarrow S_3O_6^{2-} + 2e^- \quad \text{.....(10)}$$



$$\text{.....(11)}$$

The cyclic voltammogram of fixer solution with various cut off potentials is given in Fig 1. It may be observed that when the potential was cycled between –50 to –1350 mV, two cathodic peaks (-390 & -630 mV) and two anodic peaks (-620 & -80 mV) were observed. The peak at –390 mV is ascribed to the deposition of silver and the second peak at –630 mV is due to the sulphide formation. The first peak in the reverse scan at –620 mV is due to the oxidation of sulphur compounds while the peak at –80 mV is due to the dissolution of deposited silver. It may be inferred from the above potentials that for getting pure silver with better efficiency, the deposition is to be carried out below the potential of –600 mV, as above this value, sulphiding will occur.

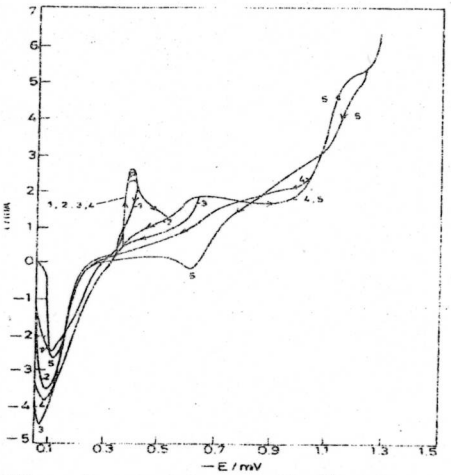


Fig. 1. Effect of potential range: Cyclic voltammograms of silver (6 g/l) containing fixer solution; scan rate: 20 mV/sec; scan range (1) -50 to 400 mV, (2) –50 to –550 mV, (3) –50 to –650 mV, (4) –50 to –1050 mV & (5) –50 to –1350 mV.

The effect of scan rate on the peak heights was studied by subjecting 6 g/l silver fixer solution to cyclic voltammetric technique which is shown in Fig 2. The potential was scanned between –50 to –500 mV. The scan rates employed were 5, 10, 20, 50 and 100 mV/sec. As the scan rate was increased the cathodic peak potential was found to be shifted to negative potentials and the anodic potential towards more positive values. Also the peak height increased with increasing scan rates.

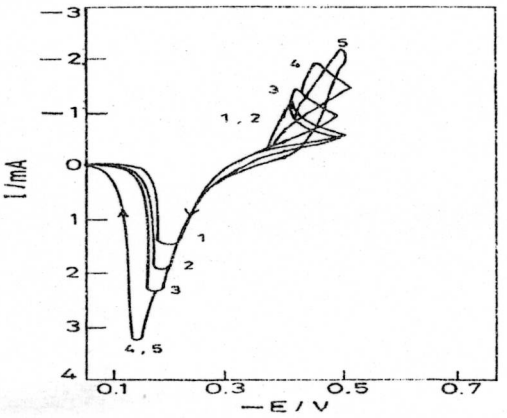


Fig. 2: Effect of sweep rate: Cyclic voltammograms of fixer solution containing 6 g/l silver; scan range: —50 to –500 mV; scan rates: (1) 5 mV/sec, (2) 10 mV/sec, (3) 20 mV/sec, (4) 50 mV/sec & (5) 100 mV/sec.

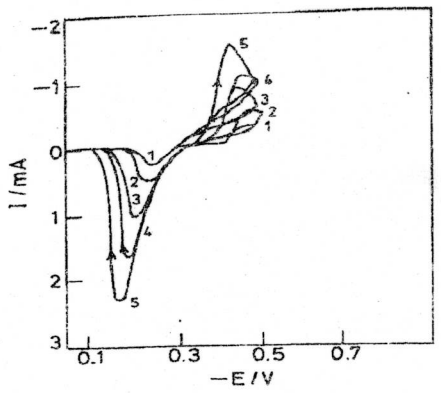


Fig.3. Effect of silver concentration: Cyclic voltammograms of fixer solution; Scan range:-50 to –500 mV; scan rate: 20 mV/ sec; silver concentration: (1) 1 g/l, (2) 2 g/l, (3) 4 g/l, (4) 6 g/l & (5) 8 g/l.

Various concentrations of silver containing fixer solutions (1-8 g/l silver fixer) were prepared and cyclic voltammetric studies were carried out using these solutions and the cyclic voltammograms obtained are shown in Fig. 3. The potential was scanned from –50 to –500 mV while the scan rate was kept at 20 mV/sec for all these solutions under investigation. As the silver concentration of fixer was increased, the peak currents were also found increasing linearly. The values of peak potentials were found to be shifted towards more positive potentials for both directions. The peak potential difference for each cyclic voltammogram was found to be greater than 200 mV indicating that these reactions are quasi reversible in nature. A graph was drawn between silver concentration and anodic peak current. It was found to be a straight line which is presented in Fig 4. Using this standard graph the silver concentration of any unknown fixer solution could be quickly estimated.

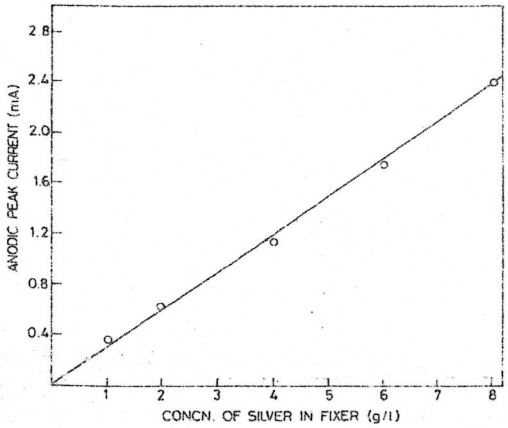


Fig. 4. Standard curve for estimation of silver concentration in the fixer solution.

Conclusion

Cyclic voltammetric technique was adopted with silver containing fixer solution to find out the optimum cathode potential for getting high pure silver deposit with better efficiency without sulphide contamination and from this studies it was found that silver is to be electrolytically recovered at less than –600 mV potential above which sulphiding will form. After optimizing the cathode potential, cyclic voltammetric studies were carried out with different silver concentrations of fixer solutions. As the silver concentration was increased the peak height was also found to be increased and hence using this technique silver concentration in any unknown fixer solution could be quickly estimated without any loss or change in the nature of the fixer solutions.

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